Attenuated Total Reflection Fourier Transform Infrared Spectroscopic Study of Dimethyl

Sulfoxide Self-Association in Acetonitrile Solutions

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W. Ronald Fawcett and Alla A. Kloss

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Attenuated Total Reflection Fourier Transform Infrared Spectroscopic Study of Dimethyl Sulfoxide Self-Association in Acetonitrile Solutions

W. Ronald Fawcett* and Alla A. Kloss

Department of Chemistry, University of California, Davis, California 95616

Abstract

Dimethyl sulfoxide solutions in acetonitrile were studied using the method of Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR FTIR) to elucidate the nature and the quantities of DMSO self-associates in solution. Results obtained are discussed together with earlier evidence of DMSO self-association in the literature. The results of the present study were used to resolve existing controversies in the assignment of bands in the DMSO vibrational spectrum. The structure of the bands due to the skeletal vibrations was found to be complex. It was shown that DMSO molecules in solution associate in cyclic dimers. Two independent calculations were performed to estimate the dimerization constant as well as the respective Gibbs free energy using the data for the SO-stretch and CSC-asymmetric stretch of DMSO.

Introduction

Dimethyl Sulfoxide (DMSO) and its aqueous solutions exhibit a number of unique properties which have found widespread use in organic chemistry, biochemistry, industry and medicine [1]. Despite rather numerous applications, the mechanism by which

the unique properties of DMSO and its solutions arise is still very poorly understood. In recent years a wide variety of theoretical and experimental studies were targeted to find an explanation for the strongly non-ideal behavior of DMSO solutions [1-8] which is revealed in many physical properties. This includes extreme deviations from additivity of density [2], viscosity [3], relative dielectric permittivity [4-5] and surface tension [4,6] observed in DMSO-water solutions. DMSO solutions violate Raoult's law even when it is a very dilute solute [7-8]. Some of its anomalous properties were attributed to the tendency of DMSO to associate[1,6-10]. For instance, enthalpies and entropies of vaporization of the pure liquid [7] exceed those of water [11], which is known to be a highly associated liquid. Furthermore, variation of the apparent dipole moment of DMSO as a function of its concentration in benzene also indicates the formation of self-associates whose polarity is different from that of the free molecule [1,4,5,12]. The structure of these associates is under dispute in the literature. It has been suggested that DMSO in solution can form either less polar cyclic dimers (Scheme 1a), or more polar chain polymers (Scheme 1b).

The most recent study of molecular association in liquid dimethyl sulfoxide and its solutions was done by Perelygin et al. [13] using Raman spectroscopy. This study is the only one to date using vibrational spectroscopy to give both qualitative and quantitative estimation of self associate formation in DMSO solutions. Perelygin et al.[13] suggested that both chains and cyclic dimers coexist in the solutions. A complex peak observed in the SO-stretching region of the DMSO spectrum in both the pure liquid and in solutions was deconvoluted into four overlapping peaks with maxima at 1027, 1044, 1058 and 1072 cm^{-1}. The band at 1027 cm^{-1} was attributed to the SO- stretching vibration of DMSO

molecules within chain polymers. The bands at 1058 and 1044 cm^{-1} were assigned to the out-of-phase and in-phase SO- stretch of molecules in cyclic dimers, respectively. The peak at 1072 cm^{-1} was attributed to the SO- stretching vibration of unassociated DMSO molecules. This interpretation of the DMSO spectrum somewhat opposes that given by other authors [7-10].

In the present paper, we reexamine the DMSO system using attenuated total reflection FTIR spectroscopy by studying the variation in band intensities with concentration for DMSO as a solute in acetonitrile.

Experimental

IR spectroscopic studies of DMSO solutions in acetonitrile were conducted with DMSO concentrations ranging from 0 to 14.04 mol/L (pure DMSO). Acetonitrile (ACN) was chosen as a solvent for DMSO self association studies because it has the smallest influence on the frequencies of all the vibrational modes of DMSO molecules [9]. Its acceptor number (the most important parameter describing intermolecular interactions in DMSO-ACN solutions [9]) is 18.9, which is very close to that of pure DMSO (19.3) [14]. This means that introduction of ACN into solution brings the least possible change of the molecular environment for DMSO as far as the solute's basic properties are involved. Furthermore, the small degree of overlap of the bands due to DMSO and ACN decreases the error involved in the spectral analysis.

For the experiments, HPLC grade DMSO and acetonitrile (Aldrich, 99.9%) were used. The residual water level in both solvents was less then 0.005%. A custom-built

ATR cell, comprised of a ZnSe crystal and a Teflon holder was mounted into a custom made variable-angle ATR accessory.

All single beam spectra were collected using the Mattson Research Series FTIR Spectrometer, with a resolution of 0.5 cm^{-1} and an incident angle of 45° in the 4000 - 550 cm^{-1} range. Absorbance spectra were referenced to that of an empty cell and were obtained from 32 parallel scans. The ATR cell was cleaned with acetone, dried in a flow of nitrogen gas and washed with the test solution before each experiment. The experiments were performed at a constant temperature of 22 °C. All the spectral manipulations were made using Spectrocalc (Galactic) or Enhanced First Fourier Infrared (Mattson) software. All the bands were assumed to be purely Lorentzian in shape.

Results and discussion.

Figure 1 shows a deconvoluted segment of the ATR FTIR spectrum of pure liquid DMSO in the range 1100-850 cm^{-1}. The DMSO molecule belongs to the C_s point group [10] so that its 24 fundamental vibrations are both Raman and IR active. This explains the close similarity of the respective spectra. However, as can be seen from Fig. 1, the curvefitting results obtained in the present study are somewhat different from those reported earlier by Perelygin et al.[13] The fit depicted in Fig. 1 has four peaks in the wavenumber range 1100 - 1000 which are observed at 1058, 1044, 1027 and 1013 cm^{-1}. The 1013 cm^{-1} peak is due to the $r_{\parallel}$ (CH$_3$) A' vibration of the DMSO molecule. The results of our recent study [9] showed that the peaks at 1058 and 1044 cm^{-1} are the only bands in

this region appearing at almost the same frequencies in both DMSO and d$_6$-DMSO in agreement with the data reported by Forrell and Tranquille [10]. Furthermore, it was shown that the band analogous to the one at 1027 cm^{-1} exists in the spectrum of gaseous DMSO [10], that it does not disappear even in very dilute solutions of DMSO, but appears at lower frequencies when DMSO is replaced with d$_6$-DMSO [9,10]. All these facts imply that this band is due to vibrations of the methyl groups, rather than related to the SO stretch of DMSO molecules associated in the chain polymers as assumed by Perelygin [13]. It was shown by the methods of both Raman and IR spectroscopy that the peak at 1058 cm^{-1} is also observed in the spectrum of gaseous DMSO [10] (at a higher frequency) and therefore cannot be attributed to self-associates of DMSO. The present study, shows the high sensitivity of the bands in the DMSO spectrum towards changes in the molecular environment and in particular the concentration of other DMSO molecules around a central one. As the concentration of dimethyl sulfoxide in a non-electrophilic solvent decreases, the 1058 cm^{-1} band (assigned to the SO- stretching vibration of unassociated DMSO molecules) shifts in the blue direction [9]. For instance, this band was observed at 1070 cm^{-1} for low DMSO concentrations in carbon tetrachloride [10].

The results of the spectral analysis presented here differ significantly from those reported by Perelygin et al. [13] who reported bands at 1072, 1058, 1044 and 1027 cm^{-1}. The main reason for the difference is the fact that these authors allowed the shape of the bands to change from purely Lorentzian to Gaussian, arguing that band shape depends on the nature of the intermolecular interactions. In this way, they were able to achieve results

in which the band positions do not depend on DMSO concentration. However, on the basis of other evidence [9,10] it is clear that the band at 1058 cm⁻¹ does shift so that Perelygin's method of data analysis gives an improper picture of the effects of intermolecular interactions.

Solvent change or dilution strongly modify the 1044 cm⁻¹ peak as well [9]. When DMSO is dissolved in organic solvents whose molecules do not interact extensively with the SO dipole of DMSO a rather intense peak at 1044 cm⁻¹ is observed [9], while in solutions of strongly electrophilic and hydrogen bonding solvents this peak diminishes and in some cases is not observed at all [9]. In the present study as well as in others [9,10] no change of this band's frequency was observed with decrease of DMSO concentration in solution. The band is rather broad, its relative intensity (with respect to that of the peak at 1058 cm⁻¹) decreases at low concentrations of DMSO, and the band totally disappears in dilute solutions. These data as well as the fact that no peak analogous to that at 1044 cm⁻¹ exists in the spectrum of gaseous DMSO indicate that this band can be attributed to the SO-stretch of DMSO self-associates.

Therefore, there is only one peak in the spectra of pure DMSO and its solutions which can be attributed to the SO stretching vibration of DMSO self associates, namely, the one observed at 1044 cm⁻¹. The stability of the frequency of this band in the entire concentration range implies that all the SO bonds in the aggregates are equally affected by the association. The frequency of the SO stretch of the DMSO molecules in the associates is significantly lower than that of the "free" ones. This indicates participation of both "S"

and "O" atoms in the association and may be attributed to the formation of cyclic dimers of DMSO (Scheme 1a). For centrally symmetric cyclic dimers one would expect to observe two bands due to the SO stretching vibrations: a symmetric (in-phase) Raman active band, and an asymmetric one (out-of-phase) active in the IR. Comparison of the Raman and IR spectra of pure liquid DMSO [10] reveals that the associate-related ν (SO) band is observed at 1044cm^{-1} in the IR spectrum, while in the Raman one it is seen at 1042 cm^{-1}. The small splitting of these bands is probably due to the absence of rigorous symmetry in the cyclic dimers.

Formation of cyclic dimers is consistent with the results of X-ray studies of the DMSO single crystal [15,16] which have shown that DMSO molecules alternate their orientation of the SO-bond along the b-axis of the crystal, and that the distance separating the sulfur and oxygen atoms in neighboring molecules is 0.25 nm . This implies antiparallel orientation of the dipoles in aggregates [8]. Molecular dynamic simulations [1,16] have shown that both the S-S and O-O radial distribution functions obtained for pure liquid DMSO have well pronounced peaks at almost the same positions (~ 0.55 nm). This indicates that DMSO molecules associate in an antiparallel fashion rather than in chains.

Assuming an equilibrium between monomers and dimers of DMSO in solution

$$2 M \rightleftharpoons D \qquad\qquad (1),$$

where M represents the monomer and D, the dimer, one can calculate the equilibrium constant as:

$$K_{dim} = \frac{C_D}{(C_M)^2} \qquad (2),$$

where C_M is the concentration of monomers and C_D, that of dimers.

By mass balance

$$C_t = C_m + 2\,C_D \qquad (3)$$

where C_t is the total concentration of DMSO molecules. After substituting equation (2),

one obtains

$$C_t = C_M + 2\,K_{dim}\,C_M{}^2 \qquad (4),$$

so that the total concentration of DMSO is a quadratic function of the concentration of

monomers. Substitution of Beer's Law ($C_M = A_M/a_M$) in (4) gives

$$C_t = A_M/a_M + 2K_{dim}\,(A_M/a_M)^2 \qquad (5),$$

where A_M and a_M are the integrated intensity and the absorbance coefficient of a band

due to a given monomer vibration. Least square analysis can be performed on the

absorbance data to fit a quadratic function from which a_M and K_{dim} can be estimated.

Alternatively, substitution of equation (2) in the mass balance equation can be done so that the total DMSO concentration will be expressed through the concentration of DMSO dimers in solution:

$$C_t = (C_D / K_{dim})^{1/2} + 2\, C_D \qquad (6)$$

After substitution of Beer's Law, one obtains

$$C_t = [A_D / (a_D K_{dim})]^{1/2} + 2\, A_D / a_D \qquad (7),$$

where A_D and a_D are the integrated intensity and the absorbance coefficient of the band due to a given dimer vibration. Consequently, a regression analysis can be performed with the absorbance data to fit a quadratic function to the data for C_t as a function of $(A_D)^{1/2}$, from which a_D and K_{dim} can be estimated.

Analysis of DMSO dimerization using equations (5) and (7) may be performed, for instance, on data for the bands at 1058 cm^{-1} (due to DMSO monomers) and at 1044 cm^{-1} (due to DMSO dimers). Curve 1 in Figure 2 shows the total concentration of DMSO in solution plotted against the integrated intensity of the band at 1058 cm^{-1}. Least square analysis gives

$$C_t = 0.274 \, A_M + 0.034 \, A_M^2 \qquad\qquad (8)$$

with a correlation coefficient $R^2 = 0.942$. The K_{dim} and a_M values calculated from these results are given in Table I.

Curve 2 in Fig.2 presents total DMSO concentration plotted versus square root of the intensity of the band at 1044 cm^{-1}. Least square analysis of these data results in

$$C_t = 1.400 \, A_D^{1/2} + 0.902 \, A_D \qquad\qquad (9),$$

with a correlation coefficient $R^2 = 0.9903$. The K_{dim} and a_D values calculated from these results are also presented in Table I. Then the concentration of dimers and monomers can be found. Calibration curves obtained for monomers and dimers of DMSO in the entire concentration range are presented in Figures 3 and 4. One can see that the results obtained are in a good agreement and consistent with reaction (1) implying formation of DMSO dimers.

Until present only two peaks in the IR spectrum of DMSO were assigned to the stretching vibrations of the skeleton of the DMSO molecule. These bands were v_a(CSC) A" and v_s(CSC) A' observed at 698 and 667 cm^{-1} respectively. However it appears that these peaks have a complex structure (Fig. 5). This may be expected because the association of the DMSO molecules into dimers should strengthen the S-C bonds in the dimerized DMSO molecules [9]. Therefore the respective bands due to the vibrations of the

DMSO molecules associated in dimers should be observed at somewhat higher frequencies than those related to monomers. The curvefitting performed on the spectra obtained in the present study lead to the unavoidable conclusion that the above bands result from overlapping peaks due to the respective vibrations of monomers and dimers of DMSO. The peak at 698 cm^{-1} is a result of superposition of the bands at 693 and 698 cm^{-1} corresponding to the ν_a(CSC) A" vibrations of monomers and dimers of DMSO respectively. Analogously the band at 667 cm^{-1} results from the overlap of the peaks at 663.7 and 668.4 cm^{-1} due to the ν_s(CSC) A' vibrations of DMSO monomers and dimers respectively. To prove the complex structure of these peaks and to verify the K_{dim} value obtained from the data for the SO-stretch, we used our data for the 693 and 698 cm^{-1} bands to calculate the dimerization constant, using equations (5) and (7) and the procedure described above. Curve 3 in Figure 2 presents total concentration of DMSO in solution plotted against integrated intensity of the band at 693 cm^{-1}. Least square analysis results in the dependence

$$C_t = 2.099 \ A_M + 1.993 \ A_M^2 \qquad\qquad (10)$$

with a correlation coefficient $R^2 = 0.990.$

A plot of the total DMSO concentration against the square root of the integrated intensity of the 698 cm^{-1} band is presented in Fig.2 (curve 4). Least square analysis of these data using equation (7) gives

$$C_t = 2.266 \ A_D^{1/2} + 2.852 \ A_D \qquad\qquad (11),$$

with a correlation coefficient $R^2 = 0.7920$. Table I shows the K_{dim}, a_M and a_D values calculated from these results. As can be seen from the Table, the values of K_{dim} calculated from the data for the ν (SO) and the ν_a(CSC) A" vibrations of both monomers and dimers are in a very good agreement. The results allow one to estimate the amounts of monomers and dimers in a solution. Figure 6 shows the percent of DMSO molecules associated in dimers plotted against the total concentration of DMSO in ACN. This dependence is consistent with the concentration pattern of the apparent dipole moment of DMSO [4,5]. Figures 3 and 4 present the calibration curves obtained for the bands due to the asymmetric stretch of the skeleton of the monomers and dimers of DMSO. One can see that results obtained are consistent with representation of the 698 cm^{-1} band as a superposition of two bands due to monomers and dimers. Because of the low intensity of the dimer related bands, results obtained from these data have a larger amount of error than those obtained from the monomer related bands. In the case of the ν_s(CSC) A' bands due to monomers and dimers, their low intensity and proximity to the cut-off frequency did not allow for another independent calculation of K_{dim}.

The Gibbs free energy of DMSO dimerization in acetonitrile was estimated using the obtained values of K_{dim} and equation

$$\Delta G^\circ = - RT \ \ln(K_{dim}) \qquad\qquad (12)$$

The results are presented in Table I. Due to the different amounts of error in the results obtained from data for different vibrations of monomers and dimers weighted averages of the values of ΔG° and K_{dim} were calculated (Table I).

It has to be pointed out that in studying the self-association of DMSO in solutions one should keep in mind that the nature of the solvent has a very strong effect on the amount of self association observed. This was demonstrated in many publications [1,5,9,10,12,17-20]. Therefore special care is needed when one makes a choice of a solvent and the DMSO concentration range for such studies. For instance, tetrachloroethylene used by Perelygin et al.[13] is a non-polar, non-electrophilic solvent; in this environment, DMSO should be more associated. Variation of DMSO concentration in such a solvent causes a dramatic change in the molecular environment. Therefore the data obtained by these authors in the 0-1.0 M concentration range cannot be extrapolated to pure DMSO where its concentration is 14.04 mol/L.

Conclusions

Analysis of the results obtained as well as the information available in the literature confirms the formation of cyclic dimers in DMSO solutions. No indication of the existence of chain polymers was found. It was shown that the 1027 cm^{-1} peak previously attributed to the SO stretching vibrations of DMSO molecules in chain polymers is not related to self-associates, but rather corresponds to vibration of the methyl groups. It was shown that the band at 698 cm^{-1} previously attributed to the $\nu_a(CSC)$ A" vibration of

DMSO results from the superposition of the bands at 693 and 698 cm^{-1} corresponding to the respective vibrations of monomers and dimers.

It was suggested that the band at 667 cm^{-1} previously attributed to the $\nu_s(CSC)$ A' vibration of DMSO results from the overlap of the bands at 663.7 and 668.4 cm^{-1} due to the respective vibration of monomers and dimers.

Independent calculations of the dimerization constant as well as the associated Gibbs energy were made using the data for ν (SO) and $\nu_a(CSC)$ A" vibrations of monomers and dimers. Results obtained are in a good agreement. The percent of the DMSO molecules associated in dimers was estimated over the entire range of DMSO concentration in acetonitrile.

Acknowledgment

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Table I. Summarized Results

Vibration data used		$\nu(SO)$ monomers	$\nu(SO)$ dimers	$\nu_a(CSC)A"$ monomers	$\nu_a(CSC)A"$ dimers	weighted average
Frequency	ν / cm^{-1}	1058	1044	693	698	—
Absorption coefficient,	a / L mol^{-1} cm^{-1}	3.7 ± 0.9	2.2 ± 0.3	0.48 ± 0.07	0.7 ± 0.2	—
Dimerization constant,	K / mol^{-1} L	0.22 ± 0.04	0.2 ± 0.1	0.23 ± 0.02	0.3 ± 0.3	0.22 ± 0.03
Gibbs free energy	$\Delta G°$ / kJ mol^{-1}	3.7 ± 0.4	4.0 ± 1.0	3.6 ± 0.2	2.0 ± 2.0	3.6 ± 0.1

Figure captions.

Figure 1. Results of the curvefit of the SO stretching region of the ATR FTIR spectrum of pure liquid DMSO showing four peaks between 1000 and 1100 cm^{-1}.

Figure 2. Plot of the total concentration of DMSO in solution against

     1- integrated intensity of the band due to the SO-stretch of DMSO monomers

     (1058 cm^{-1})

     2- square root of the integrated intensity of the band due to the SO-stretch of

     DMSO dimers (1044 cm^{-1})

     3- integrated intensity of the band due to the asymmetric CSC- stretch of DMSO

     monomers (693 cm^{-1})

     4- square root of the integrated intensity of the band due to the asymmetric

     CSC- stretch of DMSO dimers (698 cm^{-1}).

Figure 3. Plot of the integrated intensity of the band due to

     1- SO-stretch of DMSO dimers (1044 cm^{-1})

     2- asymmetric CSC- stretch of DMSO dimers (698 cm^{-1})

against the concentration of dimers in solution.

Figure 4. Plot of the integrated intensity of the band due to

      1- SO-stretch of DMSO monomers (1058 cm^{-1})

      2- asymmetric CSC- stretch of DMSO monomers (693 cm^{-1})

against the concentration of monomers in solution.

Figure 5. Results of the curvefit of the CSC stretching region of the ATR FTIR spectrum of pure liquid DMSO showing four peaks between 650 and 730 cm^{-1}.

Figure 6. Plot of the percent of the DMSO molecules associated in dimers against total concentration of DMSO in acetonitrile.
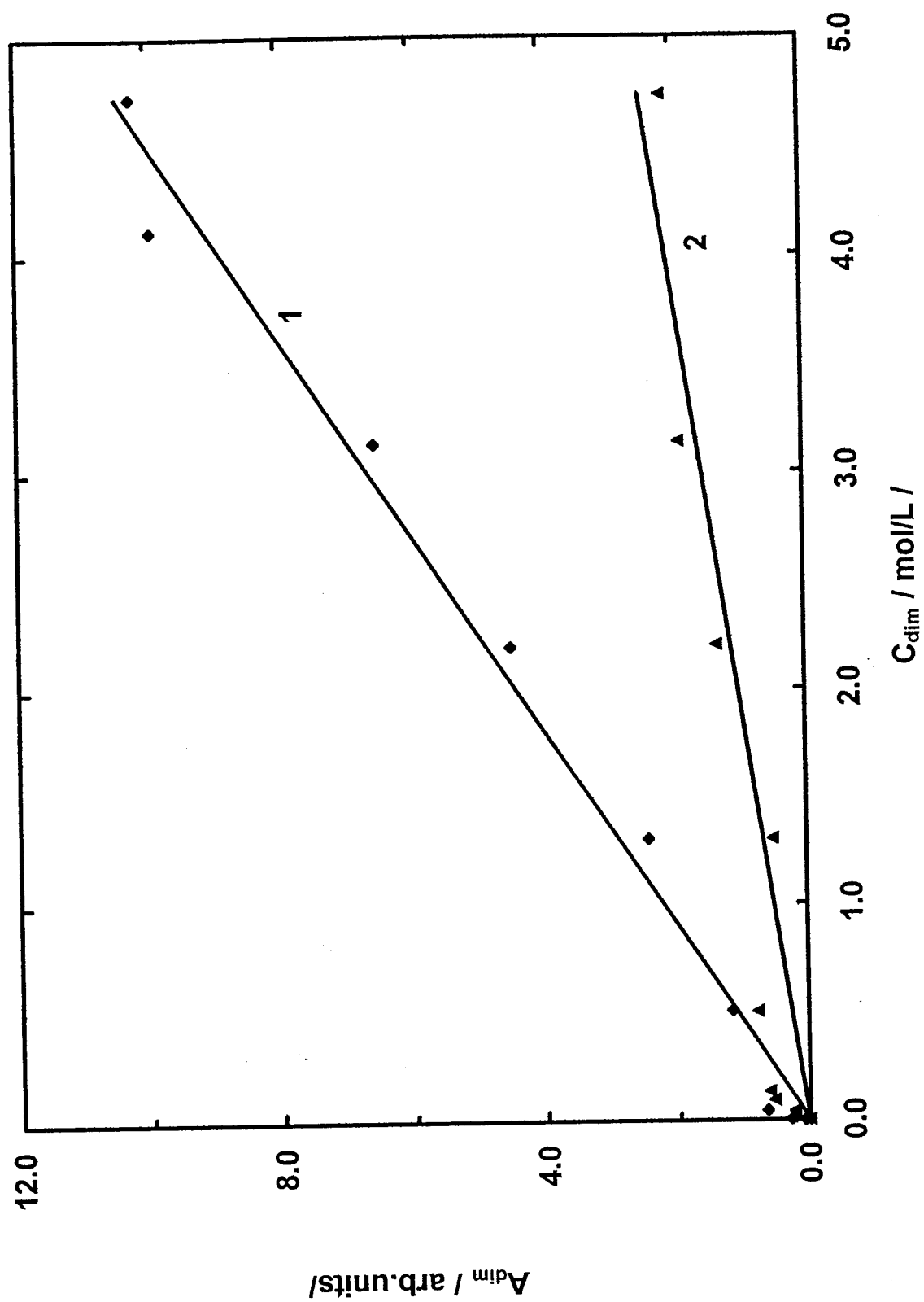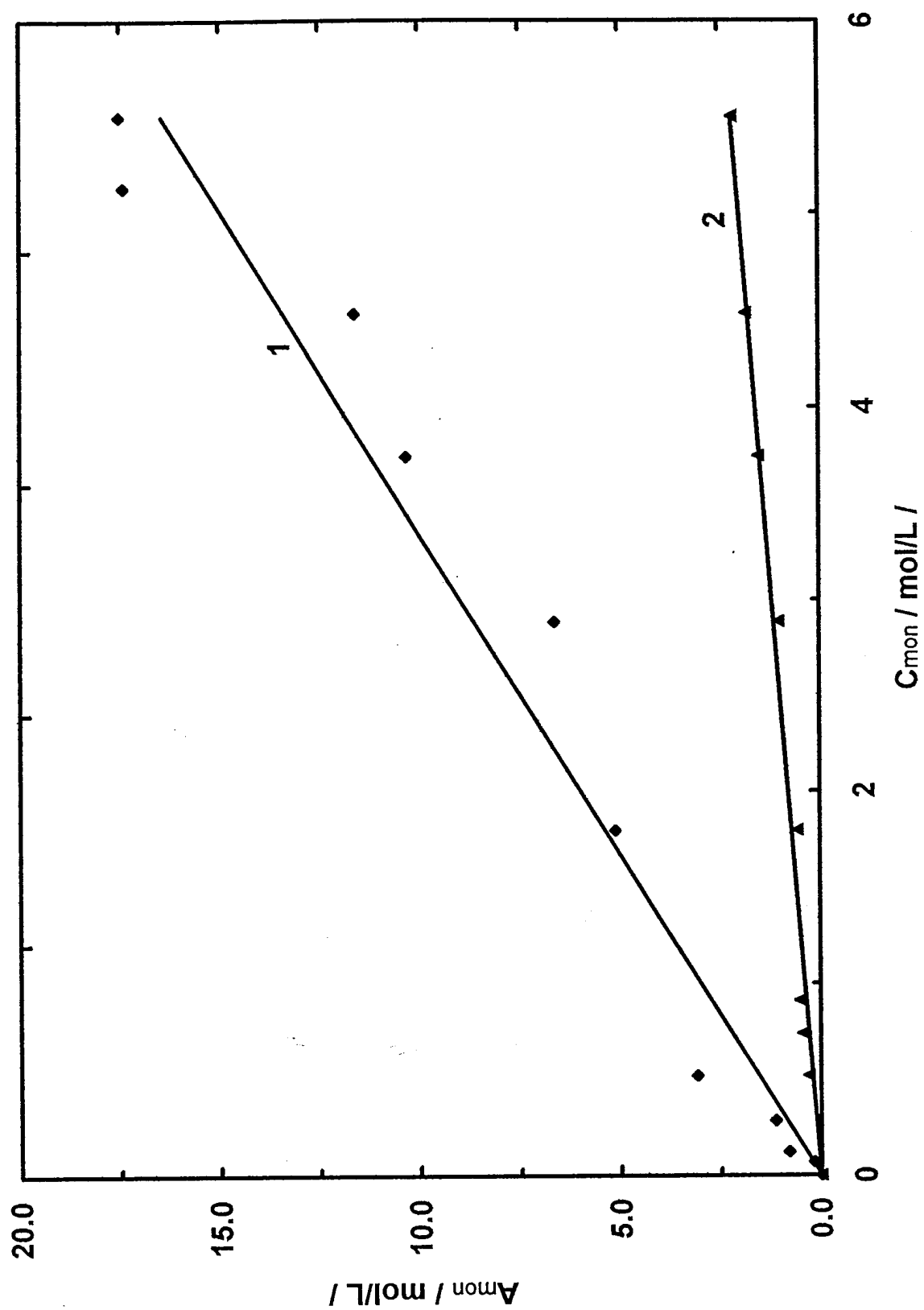
Fig. 1

Fig. 2

Fig.3

Axis labels:
- Vertical axis (left): A_{dim} / arb.units/
- Horizontal axis (bottom): C_{dim} / mol/L /

Horizontal axis values: 0.0, 1.0, 2.0, 3.0, 4.0, 5.0
Vertical axis values: 0.0, 4.0, 8.0, 12.0

Curve labels: 1, 2

Fig.4

Axis labels: A_{mon} / mol/L /, C_{mon} / mol/L /

Fig. 5

Fig. 6

% of molecules associated in dimers

C_{tot} of DMSO mol/L

Scheme 1a

Scheme 1b